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(11) **EP 0 773 269 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
14.05.1997 Bulletin 1997/20

(51) Int. Cl.<sup>6</sup>: **C09G 1/02, H01L 21/306**

(21) Application number: 96118201.1

(22) Date of filing: 13.11.1996

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: 13.11.1995 JP 317054/95  
08.04.1996 JP 110575/96

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(54) **Polishing slurry**

(57) A polishing slurry for use in chemical mechanical polishing is disclosed. The polishing slurry contains a solvent and polishing particles dispersed in this solvent. The polishing particles are selected from silicon nitride, silicon carbide, and graphite. The primary particle size of the polishing particles dispersed in the solvent is appropriately 0.01 to 1000 nm. When the polishing particles are colloidally dispersed in the solvent, the secondary particle size of the polishing particles is appropriately 60 to 300 nm.



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## Description

The present invention relates to a polishing slurry used in the fabrication of semiconductor devices and, more particularly, to a polishing slurry used in CMP (Chemical Mechanical Polishing).

Semiconductor devices such as ICs and LSIs are typically fabricated through the following steps: an integrated circuit designing step of designing integrated circuits; a photomask formation step of forming a photomask used in a lithography step; a wafer manufacturing step of manufacturing wafers having a predetermined thickness from a single-crystal ingot; a wafer processing step of forming a plurality of integrated circuits on each wafer; a dicing step of dicing each of the integrated circuits formed on the wafer into the shape of a semiconductor chip; an assembly step of packaging the diced semiconductor chips; and a testing step of testing the packaged semiconductor chips. Of these steps, the wafer processing step is most important. The wafer processing step is further subdivided into a thin film deposition step of depositing a thin film, a lithography step of exposing/developing a photoresist, an etching step of etching a wafer or the deposited thin film, and an ion implantation step of implanting an impurity ion into the wafer or the deposited thin film. These steps are done by using semiconductor fabrication apparatuses dedicated to the respective steps.

The techniques used in the etching step are roughly classified into two categories.

One is selective etching in which the target surface is masked using a photoresist and only selected portions are etched. This etching is used in the patterning of interconnections and the formation of contact holes.

The other is etch back by which a whole wafer is evenly etched. This etch back is performed to planarize the wafer surface roughened by interconnections or planarize the wafer surface after trenches or recesses are buried with a thin film. As a method of etch back, a method of performing RIE (Reactive Ion Etching) on the wafer surface after recesses on the wafer surface are buried with a photoresist is used most often (this method will be referred to as etch back-RIE hereinafter). Unfortunately, this etch back-RIE has some disadvantages that the method requires a step of coating the target surface with a photoresist, damages easily remain on the wafer surface after etch back, a dangerous etching gas is used in an RIE apparatus, and the global planarization of an entire wafer is rather low due to variations of the etching rate on the wafer surface.

In consideration of these drawbacks, CMP (Chemical Mechanical Polishing) is recently beginning to be studied in place of etch back-RIE.

In CMP, the surface to be polished of a wafer is pressed against a polishing pad adhered to a polishing disc, and the wafer and the polishing disc are rotated while a polishing agent is supplied to the polishing pad, thereby polishing the surface to be polished. The polishing agent used in CMP is a liquid prepared by dispers-

ing polishing particles which mechanically polish the surface to be polished in a polishing solution which chemically etches the surface. This liquid polishing agent has a function of setting the surface to be polished in an active state in which the surface is readily chemically polished, thereby assisting the mechanical polishing by the polishing particles. This liquid polishing agent is called a slurry.

CMP can alleviate some problems of etch back-RIE. However, although CMP can achieve high global planarization, the local planarization obtained by CMP is found to be low in fine portions of a semiconductor device structure. When the wafer surface planarized by using CMP is observed, fine micron-order dish-like recesses called "dishing" are found in fine portions of a semiconductor device structure, particularly in portions made from different substances on the wafer surface.

A typical condition in which "dishing" occurs will be described below with reference to FIGS. 1A to 1D.

FIGS. 1A to 1D are sectional views showing trench isolation steps in order.

FIG. 1A shows the state in which trenches 5 are formed in a silicon substrate 1. A polishing stopper film 2 is formed on the surface of the silicon substrate 1 except the portions in which the trenches 5 are formed. This stopper film 2 is a nitride film ( $\text{Si}_3\text{N}_4$ ).

Subsequently, as shown in FIG. 1B, silicon dioxide ( $\text{SiO}_2$ ) is deposited inside the trenches 5 and on the stopper film 2, forming an oxide film 6. The trenches 5 are buried with the oxide film 6.

In FIG. 1C, CMP is performed for the oxide film 6. As a consequence, the surface of the oxide film 6 dishes to form "dishing" 7.

In FIG. 1D, the stopper film 2 is removed.

In trench isolation in which the "dishing" 7 is formed as shown in FIGS. 1C and 1D, a conductive thin film may remain in the "dishing" 7. If a conductive thin film remains in the "dishing" 7, this film can bring about defective insulation in the future. This influences the reliability of the semiconductor device.

An important subject is to realize CMP capable of preventing "dishing".

To achieve the above subject, the inventors of this application have focused attention on polishing particles contained in a polishing slurry.

Presently, the polishing particles contained in a polishing slurry are cerium oxide particles or silica particles.

A polishing slurry (to be referred to as a polishing slurry (I) hereinafter) containing cerium oxide particles has a high polishing rate of about 0.5 to 1.0  $\mu\text{m}/\text{min}$  for an oxide film ( $\text{SiO}_2$ ) but has a low selection rate ( $\text{SiO}_2/\text{Si}_3\text{N}_4$ ) of about 2 with respect to a nitride film ( $\text{Si}_3\text{N}_4$ ) as a stopper film. Even if polysilicon (Si) is used as a stopper film, the selection rate ( $\text{SiO}_2/\text{Si}$ ) is about 1 to 2.

As described above, the polishing slurry (I) has a high polishing rate and a lower selection rate with respect to a stopper film. Accordingly, the polishing

slurry (I) readily causes overpolishing and this may scrape off a stopper film and enlarge "dishing".

In contrast, a polishing slurry (to be referred to as a polishing slurry (II) hereinafter) containing silica particles has a polishing rate of about 0.1 to 0.15  $\mu\text{m}/\text{min}$  for an oxide film ( $\text{SiO}_2$ ) which is lower than that of the polishing slurry (I). Also, when a stopper film is a nitride film ( $\text{Si}_3\text{N}_4$ ), the selection rate ( $\text{SiO}_2/\text{Si}_3\text{N}_4$ ) is about 2. Even if polysilicon (Si) is used as a stopper film, the selection rate ( $\text{SiO}_2/\text{Si}$ ) is about 1.

As described above, even the polishing slurry (II) has a low selection rate with respect to a stopper film and therefore easily causes overpolishing. However, since the polishing rate is lower than that of the polishing slurry (I), the polishing slurry (II) has the advantage that the polishing amount can be easily controlled. By controlling the polishing amount, the amount of overpolishing can be controlled and this decreases "dishing".

The polishing slurry (II) with this advantage can be preferably used in a trial manufacturing process. However, since the polishing rate is too low, the polishing time becomes too long and this makes the slurry (II) not necessarily suitable for a mass-production process.

Furthermore, both of the polishing slurries (I) and (II) have a low selection rate between the stopper film and the film to be polished. This makes a process margin difficult to allow and hence makes these slurries difficult to use in a mass-production process.

For the reasons as explained above, it is presently difficult to use CMP in a mass-production process.

In consideration of the above situation, it is an object of the present invention to provide a novel polishing slurry capable of preventing "dishing" and being preferably used in a mass-production process.

To achieve the above object, silicon nitride particles are used as polishing particles contained in a polishing slurry in the present invention.

Since silicon nitride particles are used as polishing particles contained in a polishing slurry, it is possible to obtain a polishing slurry having both a high polishing rate and a high selection rate. This polishing slurry hardly scrapes off the stopper film and can therefore prevent "dishing". This makes CMP with high local planarization feasible.

Also, since the polishing rate is high, the polishing time can be shortened and this improves the throughput of semiconductor devices. Furthermore, a high selection rate makes a process margin easy to allow. From these points of view, a polishing slurry containing silicon nitride polishing particles is suitable for a mass-production process.

It is also found that a polishing slurry containing silicon nitride polishing particles can polish metals such as copper. This is partly because the hardness of silicon nitride is comparatively high. This polishing slurry is useful in the fabrication of semiconductor devices because the polishing slurry can singly polish materials from silicon and silicon oxide to metals such as copper. For example, the number of types of polishing slurries

used in the fabrication of semiconductor devices can be decreased. When the types of polishing slurries are thus decreased, it is possible to prevent the fabrication from being complicated. This also decreases the fabrication cost of semiconductor devices.

Conventionally, polishing slurries are roughly classified into two categories: one is an oxide-based polishing slurry and the other is a metal-based polishing slurry. The oxide-based polishing slurry is represented by a polishing slurry containing silica polishing particles. The metal-based polishing slurry is represented by a polishing slurry containing alumina polishing particles. The oxide-based polishing slurry is used in polishing of silicon and silicon oxide. The metal-based polishing slurry is used in polishing of tungsten, copper, and aluminum. That is, polishing slurries are selected in accordance with the substances to be polished in the fabrication of semiconductor devices.

A polishing slurry containing silicon nitride polishing particles, however, can singly polish all of silicon, silicon oxide, tungsten, copper, and aluminum.

In addition, a polishing slurry containing silicon nitride polishing particles can polish silicides such as glass and therefore can be used in polishing of, e.g., liquid-crystal screens and lenses. This remarkably widens the range of uses of this polishing slurry.

Note that an equivalent effect can be obtained when silicon carbide or graphite, particularly carbon graphite is used instead of silicon nitride as polishing particles.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

FIGS. 1A to 1D are sectional views showing trench isolation steps;

FIG. 2 is a sectional view showing a polishing apparatus used in CMP according to the present invention;

FIGS. 3A to 3I are sectional views showing trench isolation steps according to the first embodiment of the present invention;

FIG. 4 is a graph showing the results of comparative experiments;

FIGS. 5A to 5M are sectional views showing steps of burying trenches with polysilicon according to the second embodiment of the present invention;

FIGS. 6A to 6D are sectional views showing steps of burying trenches with polysilicon;

FIGS. 7A to 7E are sectional views showing steps of forming interconnecting lines according to the third embodiment of the present invention;

FIG. 8 is a graph showing the relationship between the secondary particle size of polishing particles and the polishing rate in a polishing slurry according to the present invention;

FIG. 9 is a perspective view of another polishing apparatus used in CMP according to the present invention;

FIG. 10 is a block diagram of the other polishing apparatus used in CMP according to the present invention; and

FIG. 11 is a block diagram of an electrolytic bath of the other polishing apparatus.

Embodiments of the present invention will be described below with reference to the accompanying drawings.

FIG. 2 is a sectional view of a polishing apparatus used in CMP (Chemical Mechanical Polishing) according to the present invention.

As shown in FIG. 2, a polishing disc support 23 is arranged on a stage 21 via a bearing. A polishing disc 24 is attached to the support 23. A polishing pad 25 for polishing a wafer 20 is adhered to the polishing disc 24. A driving shaft 26 for driving the support 23 and the polishing disc 24 is connected to the central portions of the support 23 and the polishing disc 24. The shaft 26 is rotated by the rotation of a rotating belt 28. The rotating belt 28 is rotated by a motor 27.

A wafer carrier 31 is arranged in a position opposite to the polishing pad 25. A retainer ring 29 is attached to the wafer carrier 31. An adsorption pad 30 is attached to a hole formed in the retainer ring 29. The wafer 20 is adsorbed by the adsorption pad 30 by vacuum or water and carried by the wafer carrier 31. The central portion of the wafer carrier 31 is connected to a driving shaft 32 for rotating the carrier 31. The shaft 32 is rotated by a motor 33 via gears 34 and 35. The shaft 32 is attached to a driving base 36 which is attached to a piston 38 of a cylinder 37. The driving base 36 moves vertically when the piston 38 moves vertically.

To polish the wafer 20, the wafer carrier 31 carrying the wafer 20 and the polishing pad 24 are rotated. A polishing slurry is supplied to the polishing pad 25 through a polishing slurry supply nozzle 39. A down force is applied to the wafer carrier 31 by the piston 38, thereby pushing the wafer 20 against the polishing pad 25 by a predetermined pressure. The wafer 20 is polished by maintaining this state for a time required for polishing.

A method of fabricating a semiconductor device using CMP according to the present invention will be described below.

Trench isolation steps will be described first as the first embodiment. Trench isolation is accomplished by burying trenches formed in a wafer (to be referred to as a silicon substrate hereinafter) with a CVD-oxide film (CVD-SiO<sub>2</sub>) and planarizing the CVD-oxide film by CMP.

FIGS. 3A to 3I are sectional views showing the trench isolation steps in order.

As shown in FIG. 3A, silicon nitride (Si<sub>3</sub>N<sub>4</sub>) is deposited on a silicon substrate 1 to form a 70-nm thick nitride film 2. This nitride film 2 serves as a polishing stopper film. Silicon dioxide (SiO<sub>2</sub>) is deposited on the nitride film 2 to form a CVD-oxide film 3. This CVD-oxide film 3 serves as a mask when trenches are formed.

In FIG. 3B, the CVD-oxide film 3 is coated with a photoresist to form a photoresist layer 4.

In FIG. 3C, windows corresponding to a trench formation pattern are formed in the photoresist layer 4 by photolithography.

In FIG. 3D, the CVD-oxide film 3 and the nitride film 2 are etched by RIE by using the photoresist layer 4 as a mask. Thereafter, the photoresist layer 4 is removed.

In FIG. 3E, the CVD-oxide film 3 and the silicon substrate 1 are etched by RIE. As a consequence, trenches 5 are formed in the silicon substrate 1 due to the difference between the etching rates of the CVD-oxide film 3 and the silicon substrate 1. Subsequently, a damage layer formed by RIE on the surface in the trenches 5 to which the silicon substrate 1 is exposed and reaction products formed simultaneously with RIE are removed. This is done by wet processing (wet etching).

In FIG. 3F, silicon dioxide (SiO<sub>2</sub>) is deposited on the structure shown in FIG. 3E to form a CVD-oxide film 6. This CVD-oxide film 6 buries the trenches 5 and at the same time covers the surface of the silicon substrate 1 on which the trenches 5 are formed.

In FIG. 3G, CMP is performed by the polishing apparatus shown in FIG. 2 by using the CVD-oxide film 6 and the nitride film 2 as stopper films, thereby planarizing the surface of the structure shown in FIG. 3F.

In this CMP step, a novel polishing slurry according to the present invention is used. One example of the polishing slurry according to the present invention is prepared by dispersing silicon nitride particles as polishing particles in nitric acid as a solvent. The polishing particles act on the CVD-oxide film 6 and mechanically polish the CVD-oxide film 6. The particle size of the silicon nitride particles themselves, i.e., the particle size of primary particles is preferably 0.01 to 1000 nm. A particle size exceeding 1000 nm is unpreferable because the mechanical polishing properties become too strong and the chemical polishing properties become extremely weak. On the other hand, if the particle size is smaller than 0.01 nm, the mechanical polishing properties become weak to make well-balanced polishing impossible. The particle size of the primary particles is particularly preferably 10 to 40 nm. If the particle size of the primary particles is 10 to 40 nm, well-balanced polishing is possible.

The silicon nitride particles can also be colloiddally dispersed in a solvent. When the silicon nitride particles are colloiddally dispersed in a solvent, the silicon nitride particles are readily evenly dispersed in the solvent. The particle size of the colloiddal silicon nitride particles, i.e., the particle size of secondary particles is preferably 60 to 300 nm, and particularly preferably 60 to 100 nm. The particle size of the secondary particles can be measured by using a centrifugal precipitation method capable of measuring particle sizes of 0.01 μm or more.

To improve the dispersibility of polishing particles, it is also possible to further mix a dispersant such as a surfactant in a polishing slurry, in addition to colloiddally dispersing the polishing particles in a solvent.

The viscosity of the polishing slurry is preferably 1 to 10 cp. If the viscosity is low, it becomes difficult to evenly disperse silicon nitride particles, i.e., polishing particles, in a solvent. When polishing particles are evenly dispersed in a solvent, the planarity of the polishing surface can be easily improved. If the viscosity is too high, the mechanical polishing properties become strong. When the mechanical polishing properties become too strong, the warpage of a wafer or the uniformity of the thickness of a deposited film has a large effect on the planarity after CMP.

The polishing temperature is preferably 20 to 70°C. This is so because if the temperature is too high, the chemical action becomes too strong.

In this first embodiment, the polishing conditions are that the rotating speed of the polishing disc 24 is 100 rpm, the rotating speed of the wafer carrier 31 is 100 rpm, the down force applied to the wafer carrier 31 is 400 g/cm<sup>2</sup>, and the temperature of the polishing disc 24 is 25 to 30°C. The polishing slurry used consists of nitric acid as a solvent and silicon nitride particles as polishing particles and has a viscosity of 2 cp. This polishing slurry was supplied to the polishing pad at a flow rate of 300 cc/min to perform CMP on a 6" wafer (silicon substrate 1).

FIG. 3G shows the section after the polishing.

As shown in FIG. 3G, when the CVD-oxide film 6 is subjected to CMP by using the polishing slurry containing the silicon nitride particles, a processed shape having a small "dishing" and a high local planarization is obtained.

Subsequently, the nitride film 2 is etched away as shown in FIG. 3H.

In FIG. 3I, finish polishing is so performed that the surface of the silicon substrate 1 is flush with the surface of the CVD-oxide film 6. This completes trench isolation having a good processed shape with almost no "dishing" on the silicon substrate 1 and the CVD-oxide film 6 buried in the trenches 5.

FIG. 4 shows the results of experiments comparing the polishing rates, the selection rates, and the planarities of the polishing surfaces obtained by different polishing particles. Note that the polishing conditions of the comparative experiments are the same as the conditions explained with reference to FIG. 3G.

As shown in FIG. 4, a silicon dioxide film is polished by using a polishing slurry (IV) containing silicon nitride (Si<sub>3</sub>N<sub>4</sub>) particles. The polishing rate is 700 to 1000 nm/min. This polishing rate compares to or exceeds a conventionally highest polishing rate of 500 to 800 nm/min of a polishing slurry (I) containing cerium oxide (CeO) particles, and is highest among other comparative examples.

Also, a silicon dioxide film is polished with the polishing slurry (IV) by using a silicon nitride film as a stopper film. The selection rate (SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>) is 10 to 20. This selection rate far exceeds a conventionally maximum selection rate of 2 to 3 of a polishing slurry (II) containing fumed silica (fumed SiO<sub>2</sub>), and is maximum among

other comparative examples.

Furthermore, a silicon dioxide film is polished with the polishing slurry (IV) by using a silicon nitride film as a stopper film. The planarity of the polished surface is 2 to 5%. This planarity is better than a conventionally most accurate planarity of 10% of a polishing slurry (III) containing alumina (Al<sub>2</sub>O<sub>3</sub>) particles, and is most accurate among other comparative examples.

In the first embodiment as described above, it is possible by using the polishing slurry (IV) containing silicon nitride particles to simultaneously achieve high-speed polishing, a high selection rate with respect to the stopper film, and a highly accurate planarity.

To maintain the selection rate with respect to the stopper film and the planarity on the respective high levels, it is preferable to form the stopper film by using the same material, silicon nitride (Si<sub>3</sub>N<sub>4</sub>), as the polishing particles of the polishing slurry (IV) as in the first embodiment.

As the second embodiment, steps of burying trenches with polysilicon will be described below. These steps can be used to form, e.g., a memory cell of a DRAM.

FIGS. 5A to 5M are sectional views showing the steps of burying trenches with polysilicon in the order of steps.

As shown in FIG. 5A, the surface of a silicon substrate 1 is thermally oxidized to form a buffer oxide film (SiO<sub>2</sub>) 8 about 10 to 50 nm thick.

In FIG. 5B, silicon nitride (Si<sub>3</sub>N<sub>4</sub>) is deposited on the buffer oxide film 8 to form a 70-nm thick nitride film 2. This nitride film 2 serves as a polishing stopper film and an oxidation barrier film when LOCOS is performed.

In FIG. 5C, silicon dioxide (SiO<sub>2</sub>) is deposited on the nitride film 2 to form a CVD-oxide film 3. This CVD-oxide film 3 serves as a mask when trenches are formed.

In FIG. 5D, the CVD-oxide film 3 is coated with a photoresist to form a photoresist layer 9. Subsequently, windows corresponding to a trench formation pattern are formed in the photoresist layer 9 by photolithography.

In FIG. 5E, the CVD-oxide film 3, the nitride film 2, and the buffer oxide film 8 are etched by RIE by using the photoresist layer 9 as a mask, thereby exposing the surface of the silicon substrate 1. Thereafter, the photoresist layer 9 is removed.

In FIG. 5F, the CVD-oxide film 3 and the silicon substrate 1 are etched by RIE. As a consequence, trenches 10 are formed in the silicon substrate 1 due to the difference between the etching rates of the CVD-oxide film 3 and the silicon substrate 1. A damage layer formed by RIE on the silicon substrate 1 exposed to the trenches 10 and reaction products formed by RIE are removed. This is done by wet processing (wet etching). Subsequently, the surface of the silicon substrate 1 exposed inside the trenches 10 is thermally oxidized to form an oxide film (SiO<sub>2</sub>) 11.

In FIG. 5G, silicon (Si) is deposited on the structure

shown in FIG. 5F by using LPCVD, forming a polysilicon film 12. This polysilicon film 12 buries the trenches 10 and at the same time covers the surface of the silicon substrate 1 on which the trenches 10 are formed.

In FIG. 5H, the polishing apparatus shown in FIG. 2 is used to perform CMP for the polishing film 12 by using the CVD-oxide film 3 as a stopper film, thereby planarizing the surface of the structure shown in FIG. 5G (the first CMP step). This first CMP step is performed by using a polishing slurry, analogous to the polishing slurry explained in the first embodiment, which is prepared by dispersing silicon nitride particles as polishing particles in nitric acid as a solvent. Consequently, dishing formed on the exposed surface of the polysilicon film 12 can be decreased.

In FIG. 5I, the CVD-oxide film 3 is etched away by using an etching solution containing hydrofluoric acid (HF). In the structure from which the CVD-oxide film 3 is thus removed, the end portions of the polysilicon film 12 protrude from the surface of the nitride film 2.

In FIG. 5J, the polishing apparatus shown in FIG. 2 is used to perform CMP for the polysilicon film 12 by using the nitride film 2 as a stopper film, thereby planarizing the surface of the structure shown in FIG. 5I (the second CMP step). In this second CMP step, the same polishing slurry as used in the first CMP step is used. Consequently, dishing formed on the exposed surface of the polysilicon film 12 is decreased. Also, the edges of the nitride film 2 are abraded little.

In FIG. 5K, the structure shown in FIG. 5J is coated with a photoresist to form a photoresist layer 13. A portion of the photoresist layer 13 which covers a prospective element isolation region is removed by photolithography, leaving only a portion of the photoresist layer 13 which covers a prospective element region.

In FIG. 5L, the surface of the silicon substrate 1 is exposed by removing the nitride film 2 and the buffer oxide film 8 by using the photoresist layer 13 as a mask. Thereafter, the photoresist layer 13 is removed.

In FIG. 5M, the exposed surface of the silicon substrate 1 and the surface of the polysilicon film 12 are thermally oxidized by using the nitride film 2 as an oxidation barrier film, thereby forming a field oxide film ( $\text{SiO}_2$ ) 14 on the surface of the structure shown in FIG. 5L (the LOCOS step). In this LOCOS step, a bird's beak is formed along the edges of the nitride film 2. However, this bird's beak is small because the abrasion amount of the edges of the nitride film 2 is small. A bird's beak reduces the area of the element region and has an influence on the characteristics of a semiconductor device.

FIGS. 6A to 6D illustrate an example in which the fabrication method according to the second embodiment is performed by using a conventional polishing slurry. In FIGS. 6A to 6D, the same reference numerals as in FIGS. 5A to 5M denote the same parts.

FIG. 6A corresponds to the step shown in FIG. 5J.

As shown in FIG. 6A, the polishing apparatus shown in FIG. 2 is used to perform CMP for a polysilicon film 12 by using a nitride film 2 as a stopper film, thereby

planarizing the surface of the structure shown in FIG. 5I. This CMP is done by using a polishing slurry prepared by dispersing silica particles as polishing particles in nitric acid as a solvent. Consequently, dishing 7 is formed on the exposed surface of the polysilicon film 12. Also, the edges of the nitride film 2 are scraped off and abraded.

FIG. 6B corresponds to the step shown in FIG. 5K.

FIG. 6C corresponds to the step shown in FIG. 5L.

FIG. 6D corresponds to the step shown in FIG. 5M.

As shown in FIG. 6D, the exposed surface of a silicon substrate 1 and the surface of the polysilicon film 12 are thermally oxidized by using the nitride film 2 as an oxidation barrier film, thereby forming a field oxide film ( $\text{SiO}_2$ ) 14 on the surface of the structure shown in FIG. 6C. Since the edges of the nitride film 2 are largely abraded, a bird's beak largely extends in the interface between the nitride film 2 and the silicon substrate 1. This is because the abraded edges of the nitride film 2 easily warp. The bird's beak extending toward the element region reduces the area of the element region. In a certain MOSFET, the width of the element region determines the gate width of the MOSFET. In a MOSFET of this sort, the gate width is narrowed by narrowing of the width of the element region. The gate width of a MOSFET determines the drivability of the MOSFET. Accordingly, if the gate width greatly deviates from the design value, the characteristics of the semiconductor device are affected.

In contrast, in the fabrication method according to the second embodiment, the edges of the nitride film 2 are abraded little and hence do not easily warp. Accordingly, the bird's beak does not easily extend and the gate width does not largely deviate from the design value. Consequently, the characteristics of the semiconductor device are not easily affected.

Also, in the fabrication method according to the second embodiment, the conversion difference between the LOCOS patterns is small because the bird's beak is small. Accordingly, the method is suitable for fine element region patterns.

As the third embodiment, steps of forming an interconnecting pattern by trenches, burying the trenches with a conductor, and forming interconnecting lines will be described below. This interconnecting line formation method is used for high-packing-density semiconductor devices and generally called damascene process.

FIGS. 7A to 7E are sectional views showing the steps of forming interconnecting lines in order.

As shown in FIG. 7A, a CVD-oxide film ( $\text{SiO}_2$ ) 3 and a plasma oxide film ( $\text{SiO}_2$ ) 15 formed by plasma CVD are formed in this order on a silicon substrate 1. The CVD-oxide film 3 and the plasma oxide film 15 are insulating interlayers.

In FIG. 7B, the plasma oxide film 15 is so patterned as to form trenches 17 corresponding to an interconnecting pattern.

In FIG. 7C, copper (Cu) is deposited on the structure shown in FIG. 7B to form a copper film 16. This

copper film 16 buries the trenches 17 and at the same time covers the surface of the plasma oxide film 15 on which the trenches 17 are formed.

In FIG. 7D, the polishing apparatus shown in FIG. 2 is used to perform CMP for the copper film 16 by using the plasma oxide film 15 as a stopper film, thereby planarizing the surface of the structure shown in FIG. 7C. This CMP step is done by using a polishing slurry, similar to the polishing slurry explained in the first embodiment, which is prepared by dispersing silicon nitride particles as polishing particles in nitric acid as a solvent. As a consequence, dishing formed on the exposed surface of the copper film 16 is decreased. By this CMP, copper is buried only in the trenches 17 to complete buried interconnecting lines in the first layer.

Subsequently, as shown in FIG. 7E, silicon dioxide ( $\text{SiO}_2$ ) is deposited on the structure shown in FIG. 7D by using plasma CVD, forming a plasma oxide film 18. Since the surface of the structure shown in FIG. 7D is accurately planarized, the plasma oxide film 18 is easily formed.

Also, forming buried interconnecting lines using the polishing slurry according to the present invention facilitates the formation of buried interconnecting lines in the second and third layers (not shown).

The secondary particle size dependence of the polishing rate will be described below.

FIG. 8 is a graph showing the relationship between the secondary particle size of polishing particles and the polishing rate. This secondary particle size dependence of the polishing rate was obtained by polishing polysilicon with a polishing slurry prepared by dispersing silicon nitride particles as polishing particles in nitric acid as a solvent.

Referring to FIG. 8, the ordinate indicates the polishing rate and the abscissa indicates the secondary particle size.

As shown in FIG. 8, when the secondary particle size is about 50 nm, the polishing rate is 41.2 nm/min. However, when the secondary particle size exceeds about 60 nm, the polishing rate greatly increases to 810.8 nm/min. When the secondary particle size is about 200 to 260 nm, the polishing rate is 1108.4 nm/min.

As described above, a polishing slurry containing silicon nitride polishing particles has a tendency to critically increase its polishing rate when the secondary particle size of the polishing particles exceeds about 60 nm.

When the particle size of polishing particles is small, polishing proceeds mainly due to the action of chemical polishing. As the particle size of polishing particles increases, the action of mechanical polishing becomes strong in polishing. It is estimated that the action of mechanical polishing is particularly significant in a polishing slurry containing silicon nitride polishing particles when the secondary particle size is about 60 nm.

The secondary particle size is preferably as large

as possible. However, if the secondary particle size is too large, a number of flaws may be formed on the polished surface. If a conductor such as a metal enters these flaws, this may cause a short circuit. Therefore, the number of flaws is preferably as small as possible. For this reason, it is preferable that the secondary particle size do not exceed 300 nm. In addition, the particle size of secondary particles is preferably minimized as long as the polishing rate does not decrease. From these points of view, the particle size of secondary particles is particularly preferably about 60 to 100 nm.

As a solvent used in the polishing slurry of the present invention, it is possible to use an emulsifying agent, water, a surfactant, fats and oils, an adhesive, and ionized water, in addition to nitric acid. Also, an acidic solvent is primarily used as a solvent. One representative example is nitric acid. Examples of an alkaline solvent are ammonia, amines such as piperazine, and inorganic alkalis such as potassium hydroxide and sodium hydroxide. Any of these alkaline solvents can also be used as a solvent.

It is also possible to prepare a diluted polishing slurry by adding a dispersant, e.g., ionized water, to the polishing slurry according to the present invention. When a polishing slurry like this is used, not only the polishing slurry contributes to polishing but there is also an auxiliary polishing action by the dispersant. A solvent of a polishing slurry also has a dispersion effect.

Examples of the dispersant are an emulsifying agent, water, a surfactant, fats and oils, an adhesive, and ionized water (alkali ionized water and acidic ionized water).

If a polishing slurry added with a dispersant is left to stand, however, the dispersant sometimes reacts with particularly the solvent of the polishing slurry to deteriorate the polishing slurry. To prevent this deterioration of a polishing slurry, it is possible to simultaneously add a polishing slurry and a dispersant to the process point of a polishing pad when CMP is performed. Especially when a dispersant is alkali ionized water, it is preferable to produce alkali ionized water and at the same time supply the produced water together with a polishing slurry to the process point of a polishing pad. This is so because alkali ionized water cannot be stored for long time periods.

FIG. 9 is an enlarged perspective view of an essential part of a CMP apparatus (Polisher) according to a first embodiment of the invention, showing a wafer carrier 31, a polishing disc 24 and its peripheral elements.

This CMP apparatus has basically the same structure as the FIG. 2 apparatus. In the CMP apparatus of the fourth embodiment, the polishing disk 24 has a support unit (not shown) provided at a lower portion thereof, and a driving shaft (not shown) is provided at a center portion of the polishing disk 24. The polishing disc 24 rotates together with the driving shaft when a motor (not shown) rotates. A polishing pad 25 formed of polyurethane foam or polyurethane nonwoven fabric is attached to the upper surface of the polishing disc 24. A



semiconductor wafer (not shown) is held by the wafer carrier 31 by a vacuum force, etc. such that it is opposed to the polishing pad 24. A driving shaft 32 is provided on a center portion of the wafer carrier 31 for rotating the carrier 31 in accordance with the rotation of a motor (not shown). Further, the semiconductor wafer held by the wafer carrier 31 is pressed against the polishing pad 24 and released therefrom in accordance with the movement of the driving shaft 32.

In the invention, at the time of polishing a semiconductor wafer, a polishing slurry which contains silicon nitride ( $\text{Si}_3\text{N}_4$ ) particles is supplied from a polishing tank through a polishing-slurry supply pipe 39 to the polishing pad 25, and at the same time ionized water is supplied from an ionized-water supply pipe 40 to the polishing pad 25. To this end, the polishing-slurry supply pipe 39 and the ionized-water supply pipe 40 have their nozzles located above the polishing pad 25 and in the vicinity of the wafer carrier 31 which holds the semiconductor wafer. The polishing slurry and ionized water are supplied to the working area of the polishing pad 25 and mixed with each other by means of the supply pipes 39 and 40. The supply pipes 39 and 40 are movable over the polishing pad 24.

At the time of polishing, the semiconductor wafer is pressed against the polishing pad 25 on the polishing disc 24 with a down force of 50 to 500 g/cm while the pad 25 and the disc 24 rotate at 20 to 200 rpm.

Ionized water supplied from the ionized-water supply pipe 40 can be classified into alkaline ionized water and acidic ionized water. Ionized water of a desired pH is created by electrolyzing, at a low voltage, deionized water which contains no electrolyte, i.e. no metal impurity, in an electrolytic bath with a solid electrolyte contained therein. Where alkaline ionized water is used and the polishing rate is changed during polishing, the rate can be increased in a stable manner by increasing the pH value of alkaline ionized water, and can be reduced in a stable manner by reducing the pH value of alkaline ionized water. On the other hand, in the case of using acidic ionized water, the polishing rate can be increased in a stable manner by reducing the pH value of acidic ionized water, and can be reduced in a stable manner by increasing the pH value of acidic ionized water.

FIG. 10 is a sectional view, showing a CMP apparatus according to a fifth embodiment of the invention, and specifically showing a wafer carrier, a polishing disc, a waste water mechanism and an electrolytic bath for supplying ionized water. This CMP apparatus has the same basic structure as that shown in FIG. 2. A polishing pad 25 formed of polyurethane nonwoven fabric, etc. for polishing a semiconductor wafer is attached to the upper surface of a polishing disc 24. A semiconductor wafer (not shown) is held by a wafer carrier 31 by a vacuum or mater, etc. such that it is opposed to the polishing pad 25. A driving shaft 32 is provided on a center portion of the wafer carrier 31 for rotating the carrier 31 in accordance with the rotation of a motor (not shown). Further, the semiconductor wafer held by the wafer car-

rier 31 is pressed against the polishing pad 25 and released therefrom in accordance with the movement of the driving shaft 32.

At the time of polishing the semiconductor wafer, a polishing slurry containing polishing particles such as silicon nitride particles is supplied from a polishing slurry tank 41 through a polishing-slurry supply pipe 39 to the polishing pad 25, and at the same time ionized water is supplied from an ionized-water supply pipe 40 to the polishing pad 25. To this end, the polishing-slurry supply pipe 39 and the ionized-water supply pipe 40 have their nozzles located above the polishing pad 25 and in the vicinity of the wafer carrier 31 which holds the semiconductor wafer. The supply pipes 39 and 40 are disposed to be movable over the polishing pad 25, thereby supplying the polishing slurry and ionized water to the working area of the polishing pad 25 and permitting them to be mixed with each other.

The rotary polishing disc 24 is received in an envelope 43 so as to prevent the wasted polishing slurry and ionized water having been used for polishing from scattering to the outside. An exhaust port 44 is formed in the bottom of the envelope 43 for exhausting the wasted water. A wasted water pipe 45 is connected to the exhaust port 44. A one-way valve 46 is voluntarily provided across the waste pipe 45 for preventing reverse flow of the wasted water. Further, a sediment bath 47 is voluntarily provided for separating polishing particles having been used for polishing from the wasted water.

The polishing-slurry supply pipe 39 is connected to the polishing slurry tank 41, while the ionized-water supply pipe 40 is connected to an electrolytic bath 42. An ionized-water exhaust pipe 48 is connected to the wasted water pipe 45 lead from the envelope 43. A one-way valve may be provided across the ionized-water exhaust pipe 48, too.

The above-described pipe structure enables the ionized water exhausted from the electrolytic bath 42 to be mixed with the ionized water contained in the wasted water, thereby neutralizing them. Thus, the wasted pipe 45 and the ionized-water exhaust pipe 48 connected thereto constitute a neutralization mechanism. In general, when in the electrolytic bath, alkaline (or acidic) ionized water is created, acidic (or alkaline) ionized water of the same amount is also created. Therefore, in the case of performing polishing using alkaline ionized water, acidic ionized water created simultaneously and not necessary for polishing is collected through the ionized-water exhaust pipe 48 to the wasted-water pipe 45 to neutralize the wasted water created during polishing.

FIG. 11 is a sectional view of a CMP apparatus according to a sixth embodiment of the invention, showing an electrolytic bath. As is shown in FIG. 11, an electrolytic bath 42 has a cathode chamber 51 and an anode chamber 52. The cathode chamber 51 contains a cathode electrode 53, while the anode chamber 52 contains an anode electrode 54. These electrodes 53 and 54 are formed of platina or titanium. The cathode and anode chambers 51 and 52 are partitioned by a porous



barrier membrane 55 for efficiently separating negative-ionized water 63 created in the cathode chamber 51, from positive-ionized water 64 created in the anode chamber 52. The cathode electrode 53 in the electrolytic bath 42 is connected to the negative electrode 57 of a battery 56, and the anode electrode 54 to the positive electrode 58 of the battery 56.

In the electrolytic bath 42, a diluent electrolyte solution 59, with a supporting electrolyte (e.g. ammonium chloride) contained therein is mixed with deionized water, and a power voltage is applied thereto from the battery 56, thereby electrolyzing the deionized water. Negative-ionized water 63 created on the side of the cathode electrode 53 as a result of electrolyzation is alkaline ionized water, while positive-ionized water 64 created on the side of the anode electrode 54 is acidic ionized water. Moreover, if deionized water is electrolyzed in the bath 42 using oxalic acid as the supporting electrolyte, both negative-ionized water created on the side of the cathode and positive-ionized water created on the side of the anode exhibit acidic properties. The negative-ionized water 63 in the cathode chamber 51 is supplied to the outside through a negative-ionized water supply pipe 61, and the positive-ionized water in the anode chamber 52 is supplied to the outside through a positive-ionized water supply pipe 62.

Since alkaline ionized water is usually created in the cathode chamber 51, the negative-ionized water supply pipe 61 connected to the electrolytic bath 42 is used, in the sixth embodiment, as the ionized-water supply pipe 40 for supplying alkaline ionized water to the polishing pad 25, when polishing is performed using alkaline ionized water. In this case, acidic ionized water created in the anode chamber 52 is not necessary and hence exhausted. Accordingly, the positive-ionized water supply pipe 62 is used as the ionized water exhaust pipe 48 for exhausting ionized water, and connected to the wasted water pipe 45. On the other hand, if polishing is performed using acidic ionized water, the positive-ionized water supply pipe 62 connected to the electrolytic bath 42 is used as the ionized-water supply pipe 40 for supplying acidic ionized water to the polishing pad 25. In this case, alkaline ionized water created in the cathode chamber 51 is not necessary and hence exhausted. Thus, the negative-ionized water supply pipe 61 is used as the ionized water exhaust pipe 48 for exhausting ionized water, and connected to the wasted water pipe 45. (See FIG. 10)

Ionized water can be classified into alkaline ionized water and acidic ionized water. Ionized water of a desired pH is created by electrolyzing, at a low voltage, deionized water which contains no electrolyte, i.e. no metal impurity, in an electrolytic bath with a solid electrolyte contained therein. Where in the case of using alkaline ionized water, the polishing rate is changed during polishing, it can be increased in a stable manner by increasing the pH value of alkaline ionized water, and can be reduced in a stable manner by reducing the pH value of alkaline ionized water. On the other hand, in the

case of using acidic ionized water, the polishing rate can be increased in a stable manner by reducing the pH value of acidic ionized water, and can be reduced in a stable manner by increasing the pH value of acidic ionized water.

Whether alkaline ionized water or acidic ionized water is used depends upon the kind of a film deposited on a semiconductor wafer.

Ionized water can electrically stabilize the surface of the film deposited on the wafer obtained after polishing. Acidic ionized water is suitable for a deposit film made of a metal with a high melting point, such as Al, Cu, W, etc. Such a deposit film has its surface oxidized by acidic ionized water after polishing, with the result that the potential of the surface is stabilized.

Alkaline ionized water or acidic water is suitable for a deposit film made of silicon oxide ( $\text{SiO}_2$ ), silicon nitride ( $\text{Si}_3\text{N}_4$ ), polysilicon or monocrystalline silicon. Alkaline ionized water can electrically stabilize the surface of such a deposit film. Alkaline ionized water should be used case where a  $\text{SiO}_2$  film is polished, and case where a polysilicon film is polished. On the other hand, acidic ionized water should be used case where a Cu film is polished.

Conditions such as the polishing rate, the degree of stabilization of a deposit film, etc. depend upon the pH value of ionized water. Therefore, adjustment of the pH value of ionized water is very important to set optimal polishing conditions. Since the pH value of ionized water depends upon its temperature. It can be accurately adjusted by controlling the temperature of ionized water. The pH value of acidic ionized water increases as its temperature increases, whereas that of alkaline ionized water reduces as its temperature increases. Further, the rate of change in pH is higher in alkaline ionized water than in acidic ionized water.

Conventionally, polishing slurries are roughly classified into two categories: one is an oxide-based polishing slurry and the other is a metal-based polishing slurry. The oxide-based polishing slurry is represented by a polishing slurry containing silica polishing particles. The metal-based polishing slurry is represented by a polishing slurry containing alumina polishing particles. The oxide-based polishing slurry is used in polishing of silicon and silicon oxide. The metal-based polishing slurry is used in polishing of tungsten, copper, and aluminum. That is, polishing slurries are selected in accordance with the substances to be polished in the fabrication of semiconductor devices.

A polishing slurry containing silicon nitride polishing particles, however, can singly polish all of silicon, silicide silicon oxide, silicon nitride tungsten, copper, gold and aluminum.

In addition, a polishing slurry containing silicon nitride polishing particles can polish silicides such as glass and therefore can be used in polishing of, e.g., liquid-crystal screens and lenses. This remarkably widens the range of uses of this polishing slurry.

Furthermore, an equivalent effect can be obtained

by using silicon carbide or graphite, particularly carbon graphite, instead of silicon nitride, as polishing particles.

# Claims

## 1. A polishing slurry comprising:

a solvent; and  
polishing particles dispersed in said solvent  
and comprising at least one member selected  
from the group consisting of silicon nitride, sili-  
con carbide, and graphite.

2. A slurry according to claim 1, characterized in that  
a primary particle size of said polishing particles is  
0.01 to 1000 nm.

3. A slurry according to claim 1, characterized in that  
said polishing particles are colloidally dispersed in  
said solvent.

4. A slurry according to claim 3, characterized in that  
a secondary particle size of said polishing particles  
is 60 to 300 nm.

5. A slurry according to claim 1, characterized in that  
a viscosity of said solvent is 1 to 10 cp.

6. A slurry according to claim 1, characterized in that  
said solvent is acidic.

7. A slurry according to claim 6, characterized in that  
said acidic solvent is nitric acid.

8. A slurry according to claim 1, characterized in that  
said solvent is alkaline.

9. A slurry according to claim 8, characterized in that  
said alkaline solvent is one member selected from  
the group consisting of ammonia, piperazine,  
potassium hydroxide, and sodium hydroxide.

10. A slurry according to claim 1, characterized in that  
said solvent comprises at least one member  
selected from the group consisting of an emulsify-  
ing agent, water, ionized water, a surfactant, and  
fats and oils.

11. A slurry according to claim 1, characterized in that  
said solvent has a chemical etching effect.

12. A slurry according to claim 11, characterized by fur-  
ther comprising:

a dispersant added to said solvent.

13. A slurry according to claim 12, characterized in that  
said dispersant comprises at least one member  
selected from the group consisting of an emulsify-

ing agent, water, ionized water, a surfactant, and  
fats and oils.

14. A polishing slurry for use in chemical mechanical  
polishing, comprising:

a solvent; and  
polishing particles dispersed in said solvent  
and comprising at least one member selected  
from the group consisting of silicon nitride, sili-  
con carbide, and graphite.

15. A slurry according to claim 14, characterized in that  
a primary particle size of said polishing particles is  
0.01 to 1000 nm.

16. A slurry according to claim 14, characterized in that  
said polishing particles are colloidally dispersed in  
said solvent.

17. A slurry according to claim 16, characterized in that  
a secondary particle size of said polishing particles  
colloidally dispersed in said solvent is 60 to 300 nm.

18. A slurry according to claim 14, characterized in that  
a viscosity of said solvent is 1 to 10 cp.

19. A slurry according to claim 14, characterized in that  
said solvent is acidic.

20. A slurry according to claim 19, characterized in that  
said acidic solvent is nitric acid.

21. A slurry according to claim 14, characterized in that  
said solvent is alkaline.

22. A slurry according to claim 21, characterized in that  
said alkaline solvent is one member selected from  
the group consisting of ammonia, piperazine,  
potassium hydroxide, and sodium hydroxide.

23. A slurry according to claim 14, characterized in that  
said solvent comprises at least one member  
selected from the group consisting of an emulsify-  
ing agent, water, ionized water, a surfactant, and  
fats and oils.

24. A slurry according to claim 14, characterized in that  
said solvent has a chemical etching effect.

25. A slurry according to claim 24, characterized by fur-  
ther comprising:

a dispersant added to said solvent.

26. A slurry according to claim 25, characterized in that  
said dispersant comprises at least one member  
selected from the group consisting of an emulsify-  
ing agent, water, ionized water, a surfactant, and

fats and oils.

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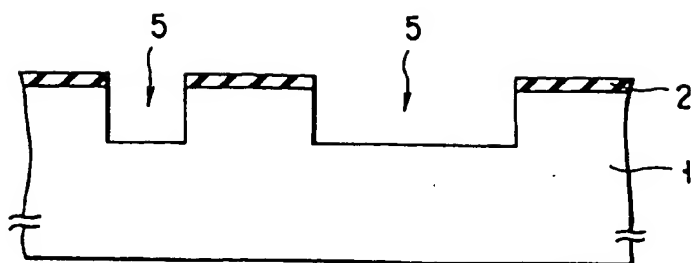


FIG. 1A

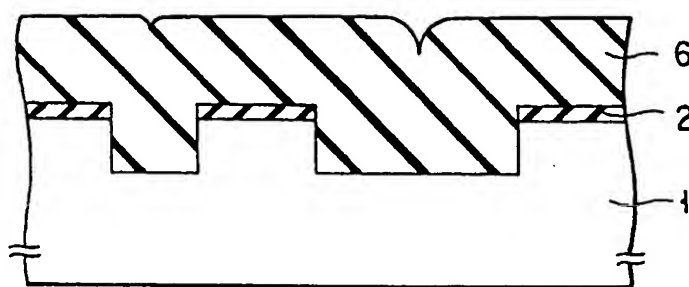


FIG. 1B

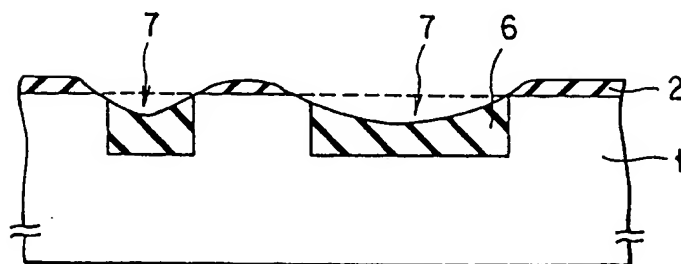


FIG. 1C

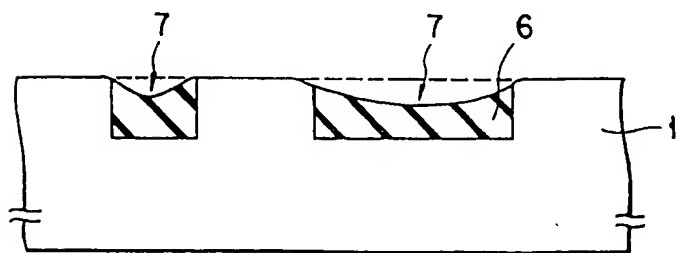


FIG. 1D

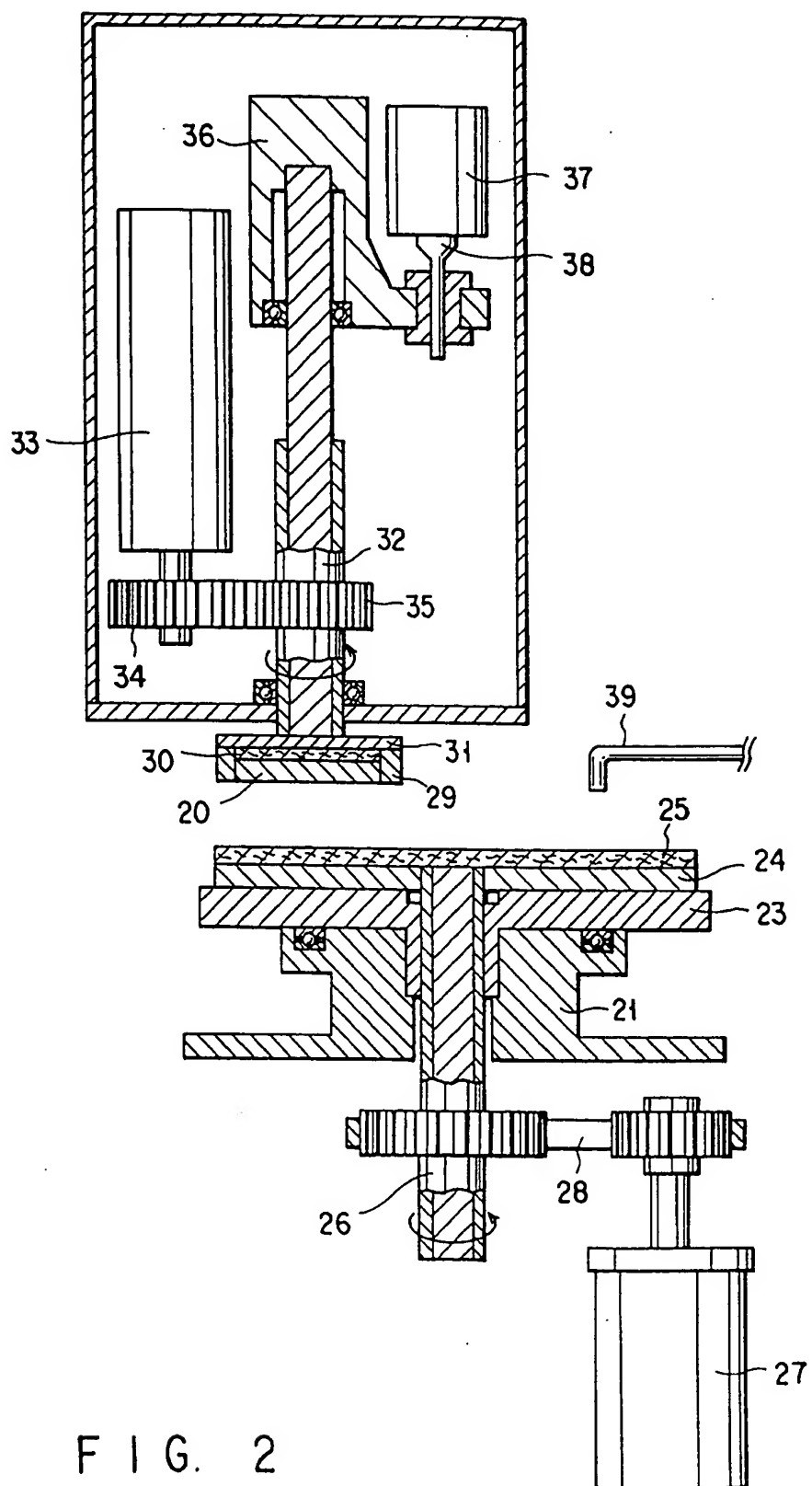


FIG. 3A

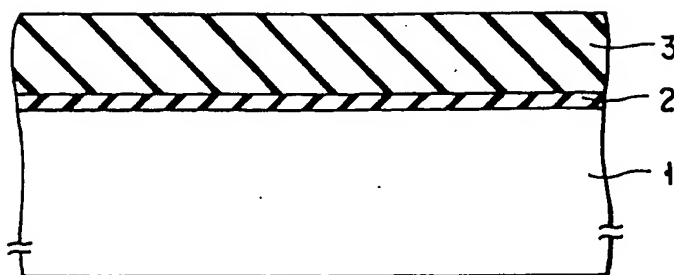


FIG. 3B

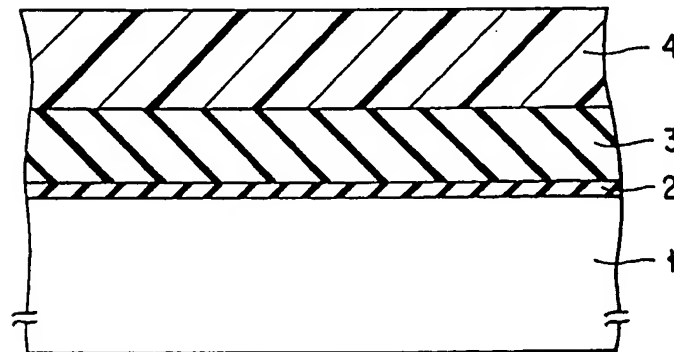


FIG. 3C

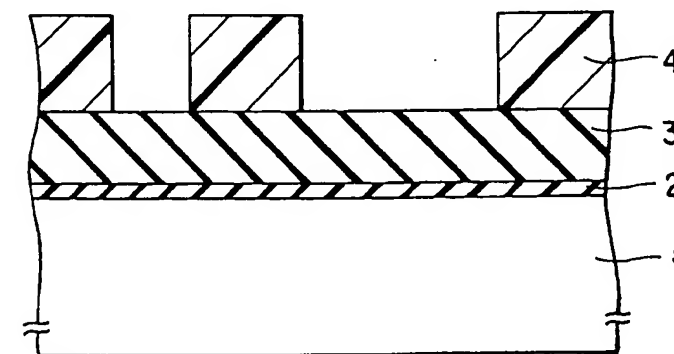


FIG. 3D

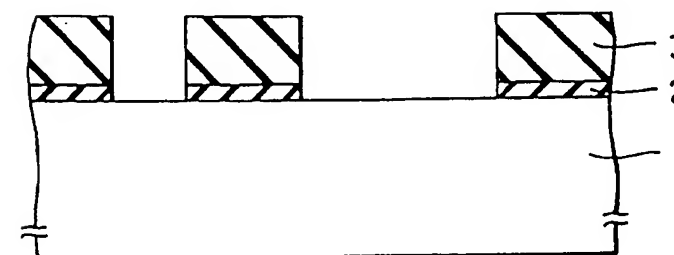


FIG. 3E

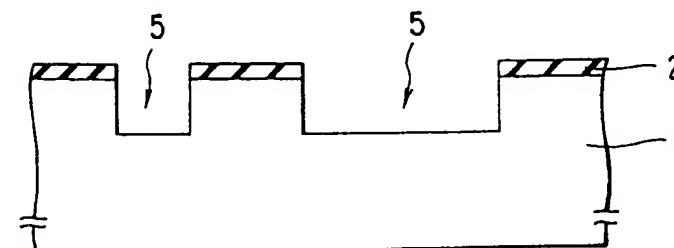


FIG. 3F

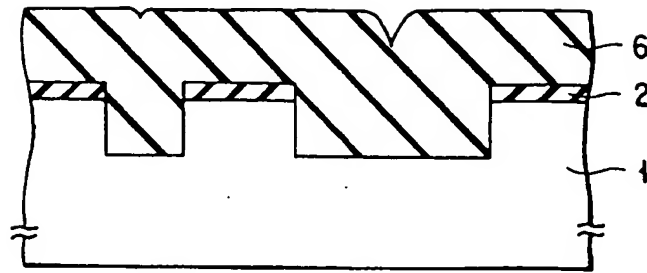


FIG. 3G

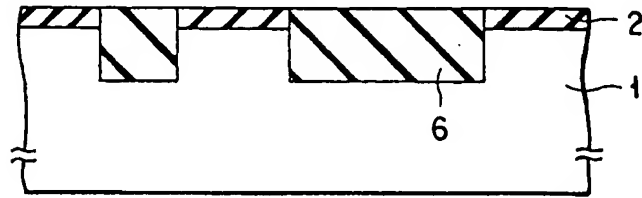


FIG. 3H

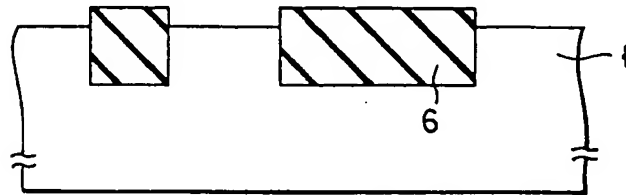
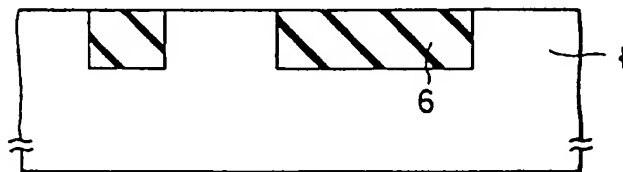


FIG. 3I



POLISHING PARTICLES	POLISHING RATE (nm / min)	SELECTION RATE (SiO <sub>2</sub> /Si <sub>3</sub> N <sub>4</sub> )	PLANARITY (%)
(I) CeO	500 ~ 800	1 ~ 3	15 ~ 20
(II) Fumed SiO <sub>2</sub>	100 ~ 110	2 ~ 3	15 ~ 20
(III) Al <sub>2</sub> O <sub>3</sub>	150 ~ 200	1	10
(IV) Si <sub>3</sub> N <sub>4</sub>	700 ~ 1000	10 ~ 20	2 ~ 5

FIG. 4



FIG. 5A

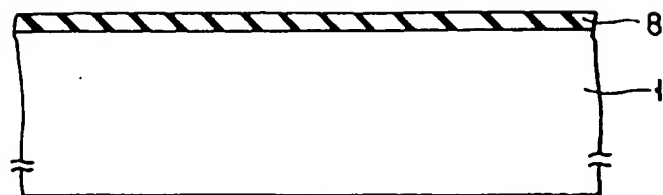


FIG. 5B

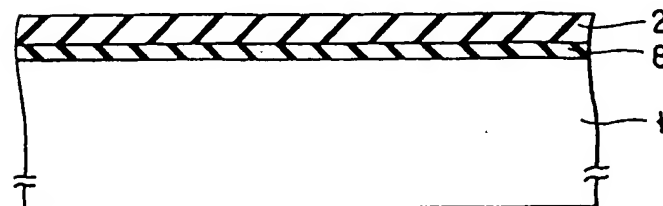


FIG. 5C

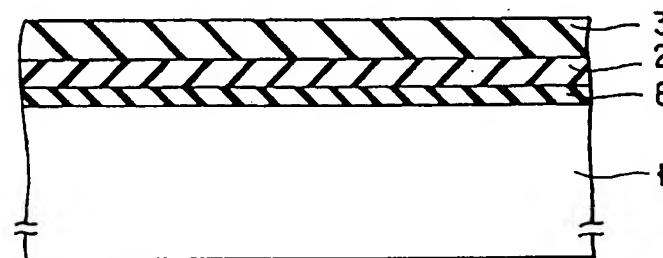


FIG. 5D

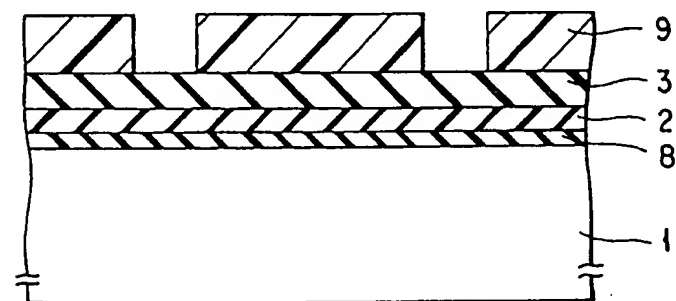


FIG. 5E

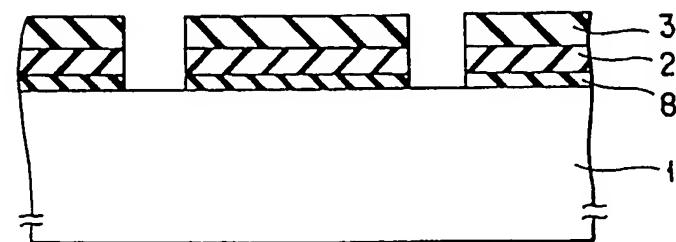


FIG. 5F

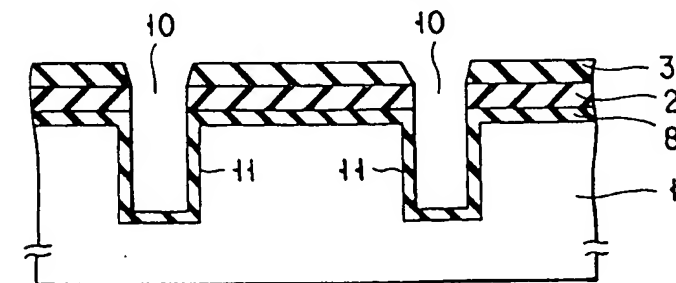


FIG. 5G

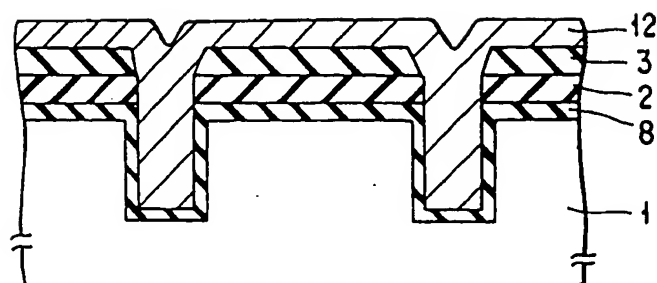


FIG. 5H

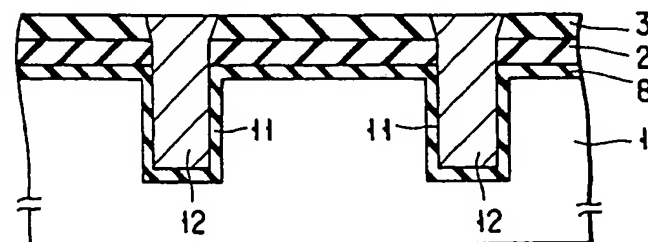


FIG. 5I

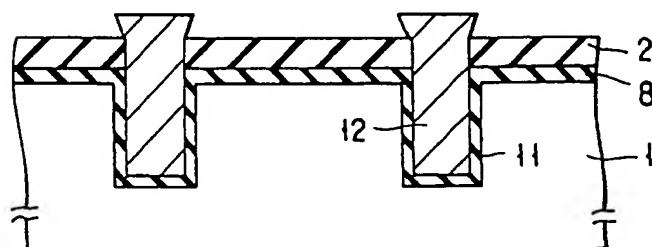


FIG. 5J

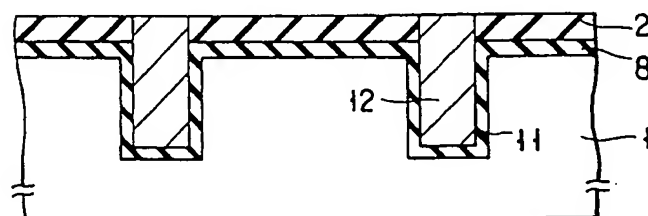


FIG. 5K

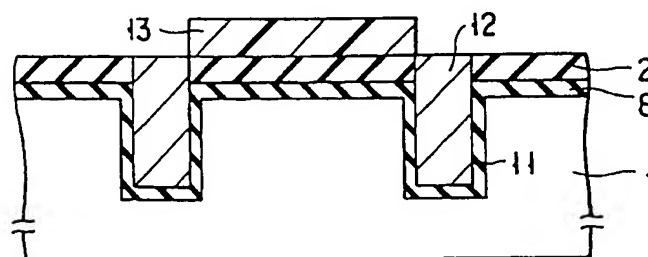


FIG. 5L

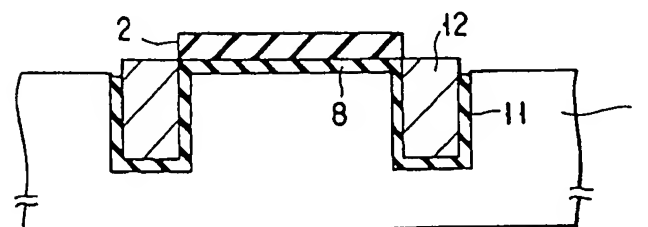


FIG. 5M

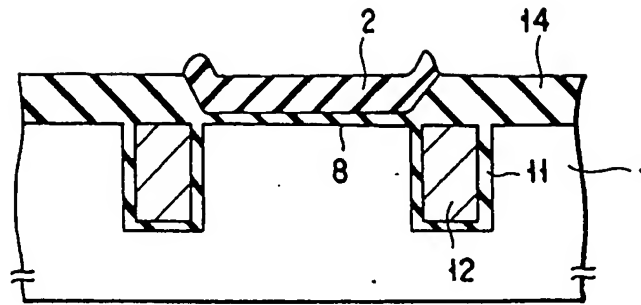


FIG. 6A

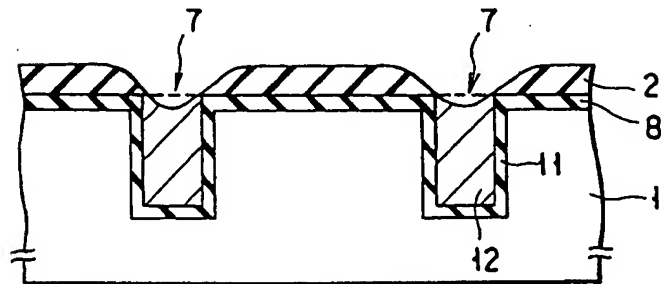


FIG. 6B

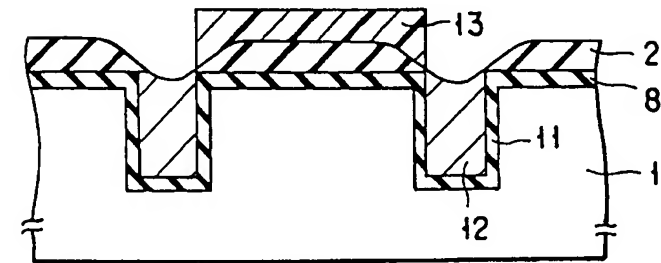


FIG. 6C

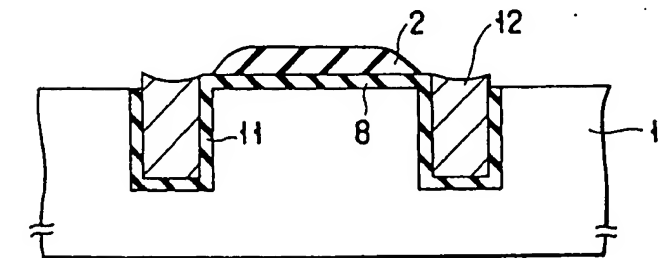
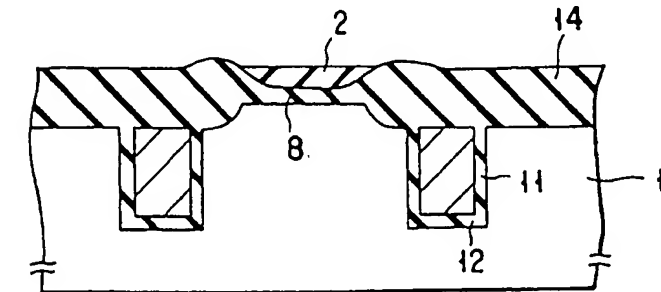
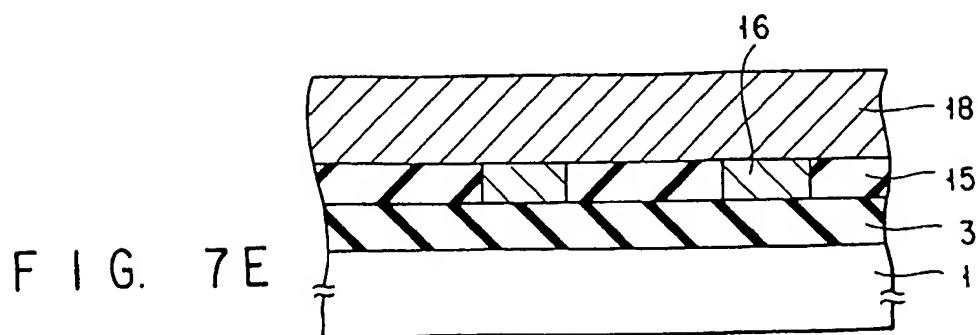
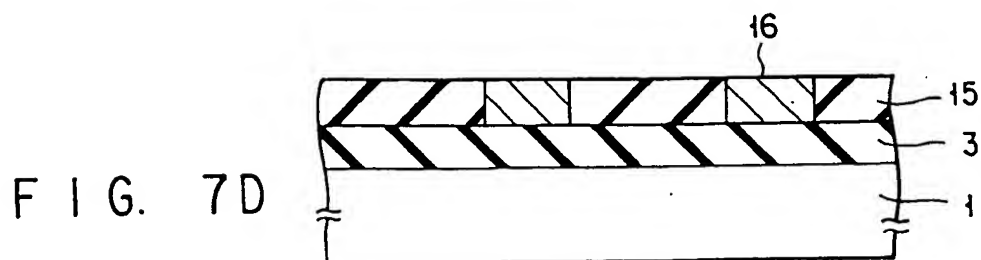
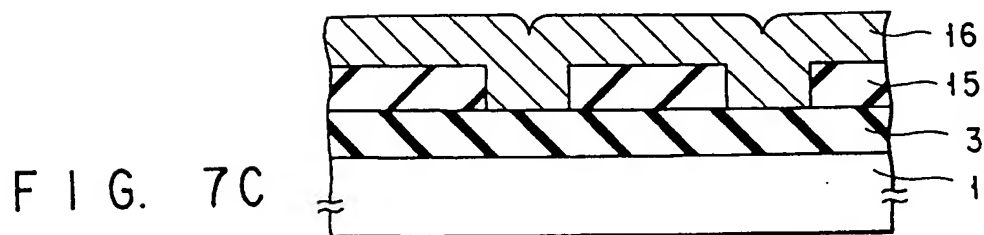
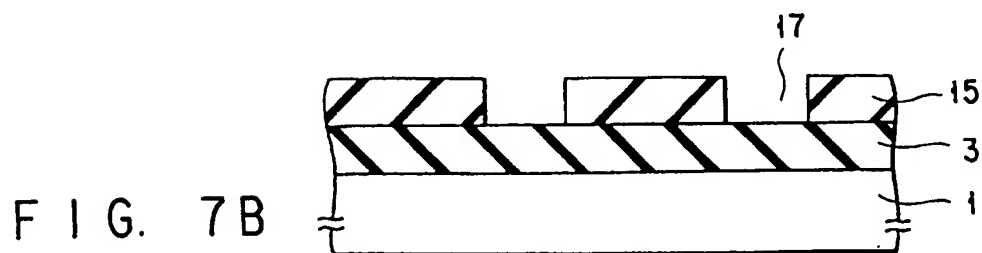
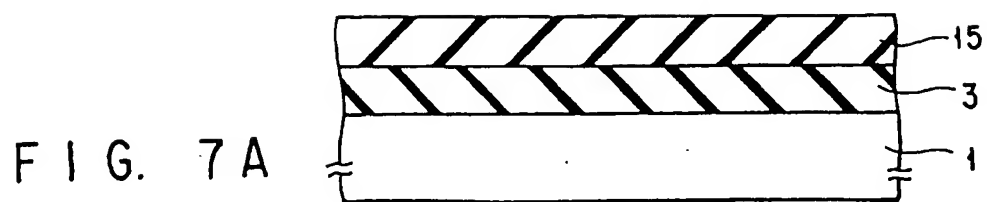


FIG. 6D





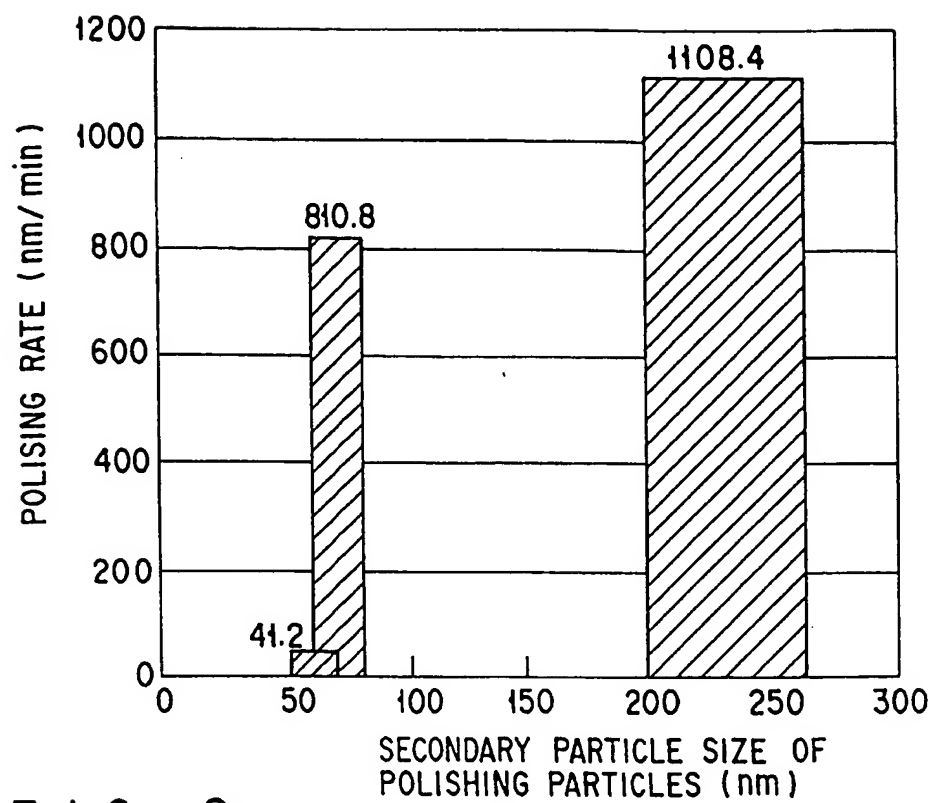


FIG. 8

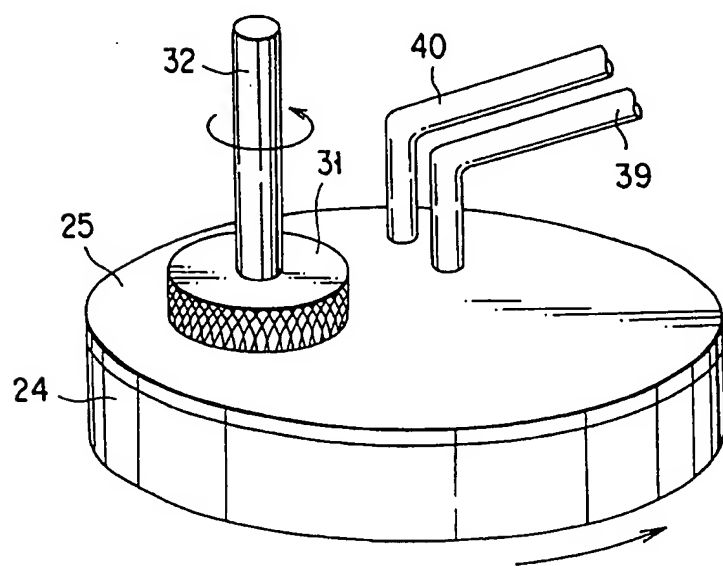


FIG. 9

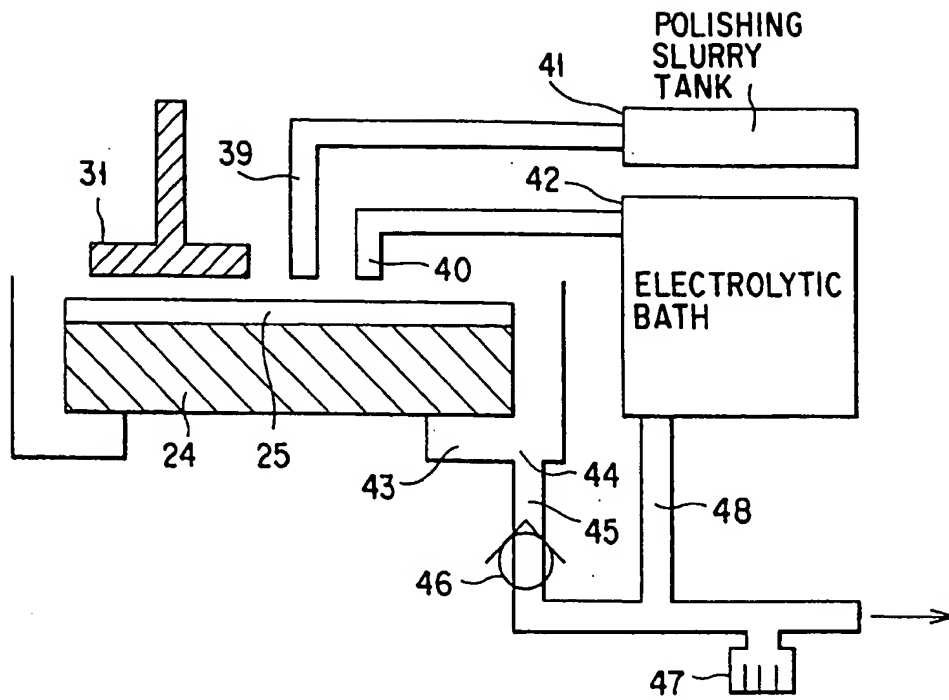


FIG. 10

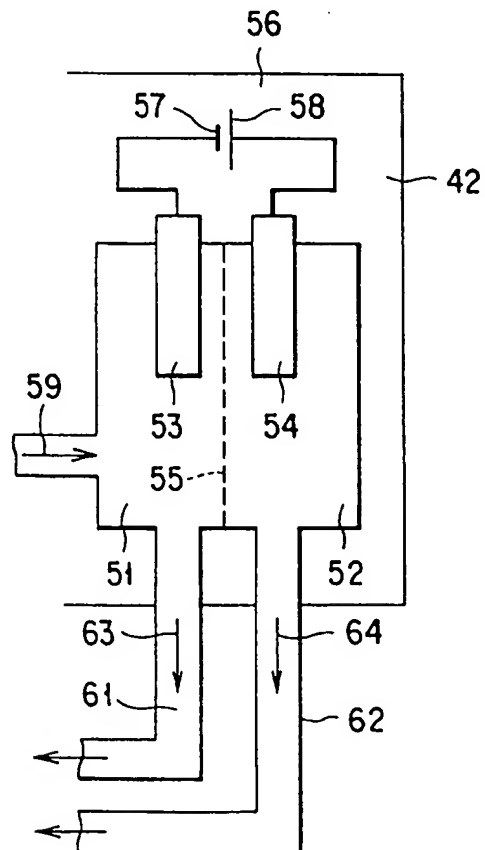


FIG. 11